Leak of gaseous VCM

13 December 2018

Saint-Fons (Rhone)

France

Heavy chemistry
Gas release
Polymerisation
Alarms
Ergonomics

THE INSTALLATIONS CONCERNED

The site:

The industrial site in question specialises in vinyl plastics, such as polyvinyl chloride (PVC), and other chemical products, such as bleach and hydrochloric acid. The site is classified as an upper-tier Seveso facility as chlorine, bleach and vinyl chloride monomer are stored there.

The site consists of:

– a polyvinyl chloride (PVC) manufacturing workshop;

– a chlorinated PVC workshop;

– third party buildings (laboratories including the Plastics Applications Laboratory (LAP, laboratoire d'applications plastiques), management offices, technical services, HSE, business centre, etc.).

The company uses vinyl chloride monomer (VCM) in both liquefied (under pressure, at ambient temperature) and gaseous forms as a raw material in the manufacture of polyvinyl chloride (PVC) by polymerisation in the reactors (pre-polymerises and autoclaves).

Physico-chemical properties and hazard classes of vinyl chloride monomer

CAS code: 75-01-4
Boiling point: -13.4 °C at atmospheric pressure
Self-ignition temperature: 472 °C
Flash point: -78 °C.
LEL = 3.6%, UEL = 33%
Classified as flammable gas (H220), pressurised gas (H280) and carcinogenic (H350)

The unit involved:

The unit involved in the accident was the PVC manufacturing facility.

For the event being studied here, this unit includes, in particular:

– a reaction zone with pre-polymerisation reactors and autoclaves in workshops Poly 3 and Poly 4;

– a VCM gas venting and condensation circuit.

The following is a simplified diagram of the elements concerned by the event which took place in the production unit: the various stages of the process involved in the event are shown in blue; in yellow, the elements that were targeted in the event:

Polymerisation → Gas venting → Condensation

Polymerisation	Gas venting	Condensation
Pre-polymerisation reactors Autoclaves Direct degassing lines Vacuum pumps	Gasometer Supply line Safety valve	Compressors Heat exchangers Bypass valves

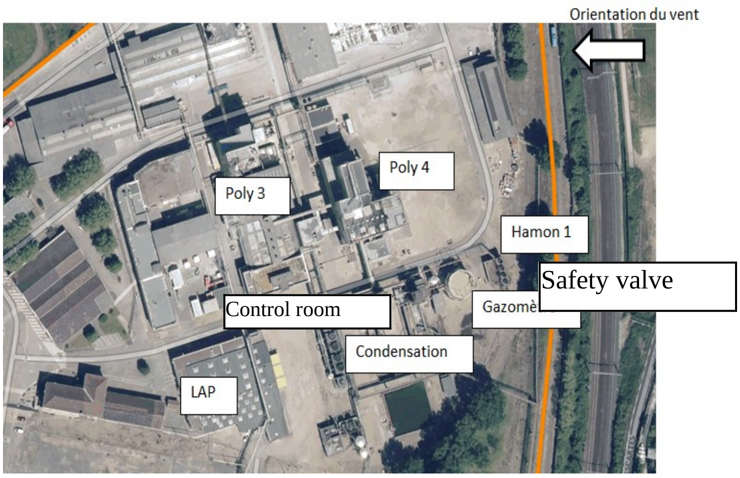


Figure 1: Aerial view of the site

Boundary of the site

During the PVC manufacturing process, at the end of the polymerisation reaction, the gas in the autoclaves is vented to discharge the VCM that has not been transformed. An initial direct gas venting operation takes place by balancing the autoclaves and the condensation unit's exchangers. The gaseous VCM remaining in the autoclaves is temporarily stored in a gasometer. After a second gas venting operation by balancing the autoclaves with the gasometer, vacuum pumps draw the content remaining in the autoclaves toward the gasometer via a supply line. This line features a safety system (servo-control) that closes the valves on the vacuum pumps' inlet and the valve upstream from the gasometer and opens the safety valve. The opening of this valve causes a release of 0.33 kg of VCM into the atmosphere at a slow rate, corresponding to the purge of the supply line. This system is triggered if one of the following conditions is met:

– the oxygen concentration in the gasometer's supply line is higher than 6%;

– if the high level or very high level in the gasometer is reached;

– if the pressure in the gasometer is high.

The gasometer acts as a buffer tank for VCM that will be conveyed via compressors to the exchangers of the condensation unit. When filled with gas, a bell rises, and when emptied, it lowers. Thus, reference is made to the level of gas in the gasometer, measured by the height of the bell. The compressors' bypass valves regulate the gas level in the gasometer. When the level rises, the compressors discharge by closing the bypass valves to convey the VCM to the condensing unit. The bypass valves open when the gasometer's level drops below 20%. The compressors can then remain in operation; the VCM circulates in a loop via the bypass valves and the level in the gasometer stops falling. As a safety measure, the compressors stop if the level reaches 15%.

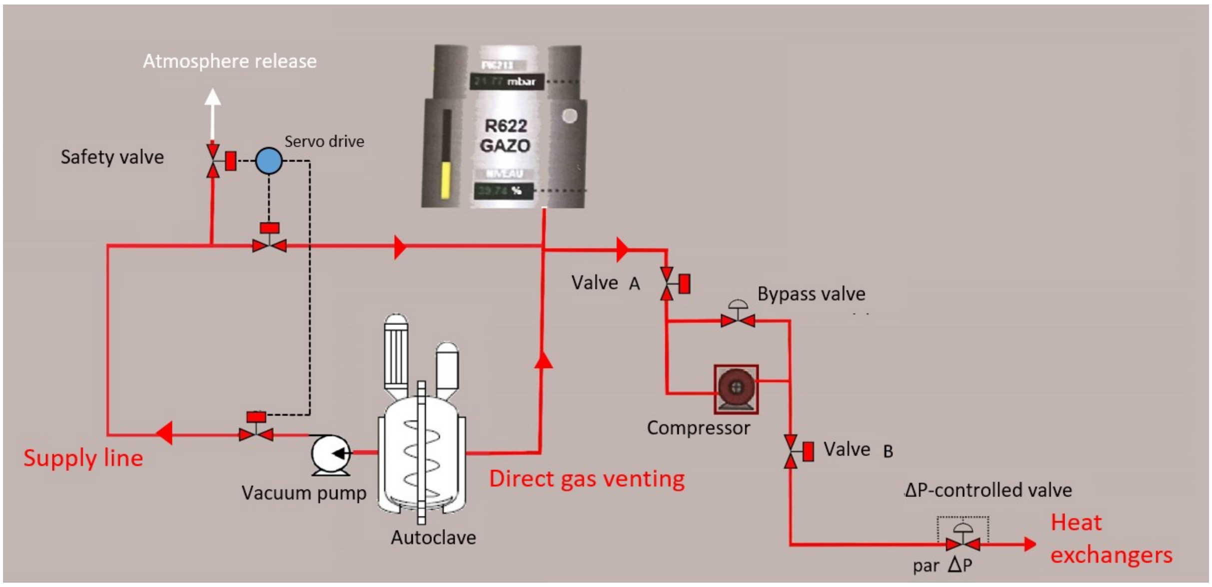


Figure 2: simplified diagram of the venting of gases to the gasometer and conveyance to the condenser

THE ACCIDENT, ITS CHRONOLOGY, EFFECTS AND CONSEQUENCES

The accident:

Hazardous phenomenon:

Between 2:25 a.m. and 9 a.m., vinyl chloride monomer (VCM) was released through the VCM gas venting system's safety valve, and the release went undetected by the operators.

Chronology of events:

At 2:25 a.m., the safety valve on the gas venting system supply line opened, allowing VCM to be released into the atmosphere for 6.5 hours. The operators did not notice the discharge: no alarm sounded to warn them that the valve was open; it was simply indicated as 'open', in green, on the mimic panel. None of the valve opening conditions described above were observed in the control room. Although the valve's status information is available on the mimic panel, it is not permanently on display in the control room.

At 2:45 a.m., the crew on duty noticed that the level of VCM in the gasometer had dropped. At 3:07, 4:36 and 4:45 a.m., the gasometer's low-level alarm (15%) sounded, causing the compressors to stop sending VCM gas to the condensers, as foreseen by the process explained above. The operators on duty suspected that the bypass valves had malfunctioned and had not opened fully, as expected upon reaching the 20% level.

The compressors would have continued to draw the VCM from the gasometer until they stopped upon reaching the 15% level. As direct gas venting (DEG 2) was in progress, the gasometer level rose automatically, and the compressors switched back on.

The crew on duty identified the problem and submitted a request for non-urgent intervention as there was no risk of VCM release, as stipulated in the "gasometer low level" alarm procedure sheet. The maintenance team became aware of the request at 7:30 a.m. and began searching for the causes of the gasometer level failure.

At 3:23 a.m., gas venting of the autoclaves began via the vacuum pumps.

A few minutes later, VCM measurements from 3 chromatographic detectors (continuous analysers), installed on the upper floor of the workshop where the autoclaves were located, showed concentrations above 5 ppm (the exposure limit value for workers is 1 ppm for 8 hours of exposure). The alarms of these detectors began sounding in the control room. At 4:26 a.m., 2 other detectors on the workshop's ground floor triggered the 5 ppm alarm, and then at 4:46 a.m., the 3 detectors on the upper level sounded again when 10 ppm was reached. As stipulated by the "search for leaks" procedure, the operators donned their gear and conducted a leak search with a portable analyser. They noted that the valves on two pieces of equipment were leaking, and suspected that a substantial leak had occurred, which, in their view, would explain the various detections. The first level maintenance crew tightened the valves, and the shift supervisor filed a request for intervention with the general maintenance department.

At around 5 a.m., detectors began to pick up VCM on the roofs of both the workshops and the laboratory. Following the "search for leaks" procedure, the operators donned their equipment and went up on the roof to identify the leak's origin.

At 6:40 a.m., a pre-polymeriser was degassed to allow maintenance to intervene on the leaky valves.

At around 8 a.m., a peak of VCM at 12 ppm was detected on the roof of the LAP. At 8:14 a.m., the control room was locked down (containment mode) following the established procedure. At 8:42 a.m., the operators stopped the degassing operations, suspecting that they were the cause of the leak. The morning shift searched for the leak's source and suspected a leak on the gasometer safety valve. Operators went to the site and observed volutes above the degassing section, which confirmed their hypothesis. At around 9 a.m., the crew on duty manually closed the safety valve which had opened unintentionally. The release of VCM was stopped.

After measuring and analysing the wind orientation, the operator concluded that the release from this valve was the cause of the various VCM detections in the workshop and on the roof.

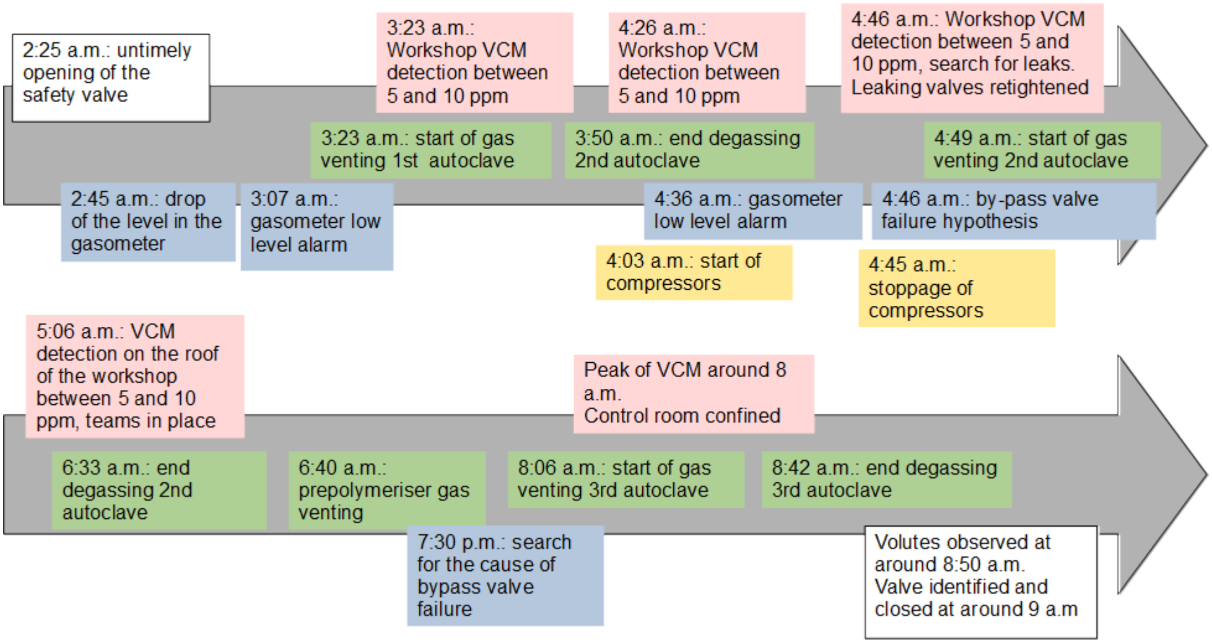


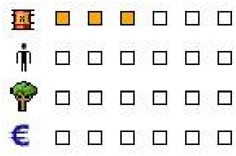
Figure 3: Chronology of the event

The consequences:

It was estimated that 3.4 t of VCM gas had been released over the 6.5 h period. Considering the wind direction (from East to West), the plume of VCM drifted inwards onto the site. There was no impact outside the site.

European scale of industrial accidents:

By applying the rating rules applicable to the 18 parameters of the scale officially adopted in February 1994 by the Member States' Competent Authority Committee for implementing the "SEVESO" Directive for hazardous substances and in light of available information, this accident can be characterised by the following 4 indices:



The substance involved, vinyl monochloride (a flammable and carcinogenic gas), can be classified under two different Seveso headings depending on whether it is in its gaseous form (4310, “upper-tier” Seveso at 50 t) or in its liquefied form (4718, “upper-tier” Seveso at 200 t). In the sectors concerned by the accident (PVC workshop, gas venting and condensation), the vinyl monochloride was in its gaseous form and was thus released into the atmosphere. The “upper-tier” Seveso heading 4310, i.e. 50 t, should thus be used to calculate the material index of the European scale of industrial accidents.

The quantity released was determined to be 3.4 t (i.e. 7% of the threshold). The index relating to hazardous materials released is thus 3 (see parameter Q1).

A health study has shown that the release had no impact on the neighbouring populations. No human and social consequences were observed concerning this accident, and the environmental consequences were not scalable. The economic consequences have not been reported to the administration.

The parameters associated with these indices and their rating scale are available at the website: http://www.aria.developpement-durable.gouv.fr.

THE ORIGIN, CAUSES AND CIRCUMSTANCES SURROUNDING THIS ACCIDENT

The origin of the release:

The cause of the event was attributed to the unintentional opening of the gas venting system due to an air supply failure. The choice of the opening mode (air fail to open) was based on a historical risk analysis. The operator does not have any internal feedback regarding unintentional opening events in its incident reports. The valve's opening is primarily associated with a risk of high oxygen content in the gasometer's supply line. It resulted in a release of 0.33 kg. This event was not monitored as the valve was not identified as a release point, but rather as safety equipment.

Following an expert evaluation, the actuator was deemed to be operating correctly. The operator's assumption of a lack of air was based on congestion forming in the valve's distribution system, notably caused by:

– humidity in the industrial air, produced and dried on-site, and supplying the valve at the end of the line;

– temperature of - 3 °C, thus limiting the flow of air; an ice plug may have formed in the line.

Unidentified risk:

The operator had not identified that the safety valve on the degassing line could be the cause of an atmospheric release of VCM, except when it is performing its safety function. It had not identified the risk of congestion that could disrupt the valve's supply system even though the servo drive was operating normally. Therefore, the scenario of a VCM release due to an unintentional opening of this valve was not considered in the hazard study.

Therefore, the valve had not been equipped with a discrepancy alarm (reporting a difference between order and actual state). The valve was displayed as “open” in green on the mimic panel, without identifying the opening order. It should have been in the closed position and displayed in red. Also, the outlet of the exhaust system was not equipped with a VCM measuring device. A study conducted in 2014 showed that the installation of a VCM detector was not possible due to humidity being present.

For ergonomic reasons, the mimic diagram showing the valve is not the main view displayed in the control room. The mimic diagrams of the autoclave lines are the views that are primarily viewed by the operators when performing their mission.

Cognitive tunnelling effect:

The release continued for 6.5 hours, as the valve involved was not immediately identified. Technical difficulties did not facilitate efforts to locate the leak: the crew on duty had focused their search on faulty bypass valves and leaky valves in the workshop.

Regarding the gasometer's low gas level, the operating crew interpreted this level as a possible failure of the compressor bypass valves. The gasometer's operating trend curve was not available in the control room. The operators had to wait for the analysis by the maintenance crew who had access to a standardised view of the process allowing for quick identification of possible failures. In addition to this, the gasometer's alarm sheet was incomplete. It indicated that only “poor compressor control” may be due to failure of the bypass valves. Experience showed that this fault had already occurred. Owing to the phenomenon known as 'cognitive tunnelling', the operators' attention remained focused on this idea.

Concerning the leaks on the valves of the two autoclaves, the crew on duty assumed that these leaks were the source of the VCM detections in the workshop.

The crew focused its attention on these leaks while following the designated procedure in this situation. VCM detections continued despite operations to retighten the leaking valves. The crew on duty, keenly aware of the risk of occupational exposure, continued to search for the leak but could not find the valve in question. As previously mentioned, it was not identified as a potential source of VCM release. 'Cognitive tunnelling' was also at issue here.

Also, the site's on-call technician had not been informed immediately of the event in progress. The alarm sheet, outlining the procedure to be followed for placing the control room in containment mode, indicates the possible leakage points to be checked. There were no specific instructions for contacting the on-call technician if VCM was detected on the laboratory's roof, where the control room's ventilation air intake is located.

ACTIONS TAKEN

The Classified Facilities Inspection authorities visited the site twice. Following the first visit, the operator was required to assess the environmental and health consequences of the event.

The second visit was conducted with BARPI representatives. The purpose of this visit was to search for the root causes of the event. During this visit, both the Classified Facilities Inspection authorities and BARPI noted that the operator had already made progress in the search efforts. However, some points still need to be examined in greater detail. The operator's responses following the inspection dealt, in particular, with the technical examination of the valve: the supplier's examination confirmed that the actuator was not faulty. Similarly, the operator revised the HAZOP (Hazard and Operability Analysis) on all the elements that could have led to the unintentional release of VCM. The additional actions undertaken following this review are presented below.

LESSONS LEARNT

The operator created a causal tree outlining the event. One of the first actions following the accident was to inform the operating crews about what had transpired while it was still fresh in everyone's mind and then again during safety rounds. To broaden feedback perspectives, special attention was given to near-accidents, including furtive or unintentional releases, for which reports were also compiled.

The operator conducted a review of “sensitive” equipment, i.e. equipment that could lead to the release of VCM into the atmosphere. HAZOPs were also conducted for the systems in which such equipment as present. Specific monitoring was established for this equipment, and a report in case of a malfunction on such equipment was requested more systematically. Complementary actions were identified at the end of the HAZOPs:

– operational or system modifications, e.g., the transmission of valve limit switch information to the control system;

– recommendations for studying possible improvements, for example, e.g. studying the possibility of closure when an air supply failure occurs on the safety valve in question.

The operator changed the valve's supply medium to nitrogen.

Following this event, the operator checked that the equipment, which is discussed in the hazard studies, is used in conditions that comply with the suppliers' recommendations.

The operator also conducted the following actions:

- a study was conducted on the possibility of installing a VCM detection system near the discharge of the safety valve on the VCM intake line on the degassing system, including an alarm in the control room and operator intervention;
- alarms were added on valves that could be a source of VCM release. As a result, various “alarm procedure” sheets were reviewed or created;
- displays on the process monitoring software were standardised for easier identification of possible failures;
- information was added to the displays of the gasometer mimic panels and on the screens in the control room, including a review of the informal training module;
- the procedure for contacting the site's on-call technician was updated.

Safety rounds were organised to present these various modifications to the employees. All of the players were involved in implementing these changes, and a mentoring was established to keep in mind the history of changes undertaken throughout the installations.

The operator's challenge is to render the feedback from this event sustainable over time and prevent it from happening again. To this end, the causes of the event were recorded. In the second half of 2019, the operating crews were again reminded of the importance of taking a step back to reassess the situation, the environmental consequences and the actions taken. For this type of event, it seems necessary not to forget the event and to share the experience of those who lived through the accident. Everyone's knowledge about the life of the installation should be maintained.